# *Chemical Equilibria & the Application of Le Châtelier's Principle to General Equilibria*

CHEM 102H

T. Hughbanks

---

# *Example of Equilibrium*

$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$$

- Reactions can occur, in principle, in either direction.
- When the rate of the forward and reverse reactions become equal, the system is said to be in (dynamic) equilibrium.
- Set up an equation to find the equilibrium concentrations.

---

$$\alpha A(g) + \beta B(g) \rightleftharpoons \gamma C(g) + \delta D(g)$$

- Recall our "thin-air" equation (page 335):

$$G_m(J) = G^\circ(J) + RT \ln P$$

\- applies to each gas (J) involved in the equilibrium

- We can use separate expressions for each gas to derive

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$

- where $Q$ is the reaction quotient:

$$Q = \frac{P_C^\gamma\, P_D^\delta}{P_A^\alpha\, P_B^\beta}$$

$$\alpha \mathrm{A}(g) + \beta \mathrm{B}(g) \rightleftharpoons \gamma \mathrm{C}(g) + \delta \mathrm{D}(g)$$

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$

When the reaction has “come to equilibrium”, no net changes in pressures of reactants or products occur. At that point, $\Delta G_{rxn} = 0$, and Q becomes equal to $K_{eq}$.

$$\Delta G^\circ_{rxn} = -RT\ln K_{eq}$$

- where $K_{eq}$ has the same form as the reaction quotient, but the pressures must satisfy the constraint:

$$K_{eq} = \frac{P_C^\gamma \, P_D^\delta}{P_A^\alpha \, P_B^\beta}$$

pressures are values *at equilibrium*

---

## General Expressions for $K_{eq}$

$$\alpha \mathrm{A}(g) + \beta \mathrm{B}(g) \rightleftharpoons \gamma \mathrm{C}(g) + \delta \mathrm{D}(g)$$

- In general, the equilibrium constant is defined using *activities* (no units):

$$Q = \frac{a_C^\gamma \, a_D^\delta}{a_A^\alpha \, a_B^\beta} \qquad K_{eq} = \frac{a_C^\gamma \, a_D^\delta}{a_A^\alpha \, a_B^\beta}$$

*equilibrium* values

for *gases*, **pressures** (bars) ≈ **activities**. For species in *dilute solutions* **concentrations** (M) ≈ **activities**:

$$K_{eq} \approx \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

, but w/o units

---

## Equilibrium Probs - General Approach

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}}$$

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$

- If $\Delta G_{rxn}$ is negative, the reaction will “go forward” to form more products. $Q$ will therefore get bigger (until it reaches $K_{eq}$).
- If $\Delta G_{rxn}$ is positive, the reaction will “go in reverse” to form more reactants. $Q$ will therefore get smaller (until it reaches Keq).

## Standard States $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$

- 298 K, 1 atm. Each gas phase reactant and product considered to be at 1 atm. pressure under standard conditions. (eg., if A & C are gases, $P_A = P_C$ = 1atm)

Example: $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

from data in Appendix 2 (all in kJ):
$\Delta G°_{rxn}$= -202.87 - (-16.45) - (-95.30) = - 91.12 kJ
This is ΔG for converting 1 mol $NH_3$ and 1 mol HCl at 1.0 atm. pressure into solid $NH_4Cl$ — at 298 K.

---

## Example: Haber Process

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

- 1.00 mol $N_2$, 3.00 mol $H_2$, and 0.500 mol $NH_3$ are placed in a 50.0 L vessel at 400 °C. At this T, $K_C$ = 0.500.

1. Will more $NH_3$ form, or will $NH_3$ dissociate to form more $N_2$ and $H_2$?
2. Set up an equation to find the equilibrium concentrations.

---

## Haber Process - answer, 1st part

- Compare the value of Q with $K_C$

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.01)^2}{(0.02)(0.06)^3} = 23.15$$

- This is larger than 0.50 so rxn. shifts left
- $[NH_3]$ will decrease from its initial value, $[H_2]$ and $[N_2]$ will increase.

## *Haber Process - answer, 2nd part*

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

<u>define</u> x as the amount that $[NH_3]$ decreases:

initial: 0.02M 0.06M 0.01M

change: +(1/2)x +(3/2)x -x

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.01 - x)^2}{(0.02 + x/2)(0.06 + 3x/2)^3}$$

$$0.500 = \frac{(0.01 - x)^2}{(0.02 + x/2)(0.06 + 3x/2)^3} \Rightarrow x \approx .0079$$

(Solution found graphically)

## *Different Forms of $K_{eq}$: $K_C$ vs $K_P$*

- In the preceding example we used "$K_C$" - the eq. constant expressed in concentrations. How is this related to "$K_P$" - the eq. constant expressed in pressures?
- Ans.: For this example, $K = K_P = (RT)^{-2} K_C$ $= [(0.08314)(673)]^{-2}(0.5) = 1.6 \times 10^{-4}$

  (Note the value for R was in "L• bar/mol$^{-1}$K$^{-1}$")
- In general, $K_P = (RT)^{\Delta n} K_C$
- Remember, $K_P$ is the "thermodynamic equilibrium constant", K

## *Mond Process - Another Look*

$$Ni(s) + 4\,CO(g) \rightleftharpoons Ni(CO)_4(g)$$

- From our earlier problem, ΔH˚ = –160.8 kJ and ΔS˚ = –409.5 J/K
- Suppose that 0.05 mol of $Ni(CO)_4$ is introduced into a 1.0 L flask.

1. What are the pressures of $Ni(CO)_4$ and CO at 300K?
2. What are the pressures of $Ni(CO)_4$ and CO at 500K?

# *Mond Process - Another Look*

$$\mathrm{Ni}(s) + 4\ \mathrm{CO}(g) \rightleftharpoons \mathrm{Ni(CO)_4}(g)$$

$K_{300}$ = exp{–[–160,800/300 – (–409.5)]/(8.314)}
= $e^{15.21}$ = 4.05 × $10^{6}$
$K_{500}$ = exp{–[–160,800/500 – (–409.5)]/(8.314)}
= $e^{-10.57}$ = 2.56 × $10^{-5}$

<u>Initial</u> pressures:
$P_{300,\mathrm{Ni(CO)4}}$ = 1.25 bar
$P_{500,\mathrm{Ni(CO)4}}$ = 2.08 bar

---

# *Mond Process - answers, 2<sup>nd</sup> part*

$$\mathrm{Ni}(s) + 4\ \mathrm{CO}(g) \rightleftharpoons \mathrm{Ni(CO)_4}(g)$$

<u>define</u> x as the amount that $P_{\mathrm{Ni(CO)4}}$ decreases:

| | | |
|---|---|---|
| initial: | 0.0 | 1.25 |
| change: | +4x | -x |

$$K_P(300) = \frac{\mathrm{P_{Ni(CO)_4}}}{\mathrm{P_{CO}^4}} = \frac{1.25\text{-}x}{(4x)^4}\ ;\ K_P(500) = \frac{\mathrm{P_{Ni(CO)_4}}}{\mathrm{P_{CO}^4}} = \frac{2.08\text{-}x}{(4x)^4}$$

$$4.05 \times 10^{6} = \frac{1.25\text{-}x}{256x^4} \quad \Rightarrow x \approx .0056 \quad P_{\mathrm{CO}} = .0224 \text{ bar}$$

$$2.56 \times 10^{-5} = \frac{2.08\text{-}x}{256x^4} \quad \Rightarrow x \approx 1.9794 \quad P_{\mathrm{Ni(CO)_4}} = 0.1006 \text{ bar}$$

$$P_{\mathrm{CO}} = 7.9176 \text{ bar}$$

---

# *Le Châtelier's Principle*

- "When a change is imposed on a system at equilibrium, the system will react in the direction that reduces the amount of change."
- "Changes" include adding or removing material, or changes in pressure or temperature.

## *Response of Equilibria to Changes*

- Easy to predict effect of concentration changes - look at *Q*.
  - Example: consider adding 0.05 mol $Cl_2$ to the to this system, prepared by putting 0.05 mol of $PCl_5$ into a 1.0 L flask already at equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad K = 78.3 \ \text{(at 250 °C)}$$

| | | | | |
|---|---|---|---|---|
| P | x | x | 2.174 - x | |
| $P_{eq}$ | .1799 | .1799 | 2.5341 | ⇔ (x = 0.1799) |
| | | +2.714 | | added pressure |
| $P_{eq}$ | .1799-y | 2.8939-y | 2.5341+y | ⇔ (x = 0.1799) |

## *More: Le Châtelier's Principle*

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

- An equilibrium mixture at 1200 K contains 0.613 mol CO, 1.839 mol $H_2$, 0.387 mol $CH_4$ and 0.387 mol $H_2O$, all in a 10.0 L vessel. (What is $K_C$?)
- All of the $H_2O$ is somehow removed, and equilibrium is re-established.
- What will happen to the amount of $CH_4$?
- Set up eqn. for final amount of $CH_4$.

## *Using Le Châtelier's Principle - Set up*

$$K_C = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

| | | | | | |
|---|---|---|---|---|---|
| init. | .0613 | .1839 | .0387 | .0387 | M |
| chg. | .0613 | .1839 | .0387 | 0.0 | M |

- Equilibrium is re-established by production of more $H_2O$ (let the final $[H_2O]$ = *x*):

| | | | | | |
|---|---|---|---|---|---|
| fin. | .0613-*x* | .1839-3*x* | .0387+*x* | *x* | M |

## *Using Le Châtelier's Principle - Set up*

$$K_{eq} = 3.93 = \frac{(.0387 + x)x}{(.1839 - 3x)^3(.0613 - x)}$$

## *Changes in Temperature*

- The equilibrium “constant” is not constant with temperature.

Le Châtelier’s Principle would suggest:

- Qualitatively, if a reaction is endothermic then the equilibrium “constant” increases with temperature
- If a reaction is exothermic then the equilibrium “constant” decreases with temperature

## *Effect of Temperature on Equilibria*

We have already seen the key relationship:

$$\Delta G^\circ_{rxn} = -\,RT\ln K_{eq}$$

Solve for $K_{eq}$ and use $\Delta G \approx \Delta H^\circ - T\Delta S^\circ$:

$$\ln K(T) = \frac{-\Delta G}{RT} \cong -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

or, comparing two temperatures:

$$\ln\frac{K_2}{K_1} \cong \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Leftrightarrow \text{van't Hoff eqn.}$$

## Changes in Pressure

- Consider (significant at 700 ˚C):

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s)$$

Le Châtelier’s Principle would suggest:

- If the pressure is suddenly increased, say by suddenly compressing the container, more $CO_2$ would react with CaO to produce more $CaCO_3$.

## Changes in Pressure

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s)$$

$$\Delta H^\circ = +178.3 \text{ kJ};\ \Delta S^\circ = -160.59 \text{ J/K}$$

- Estimate the temperature at which $CaCO_3$ decomposes under normal conditions. (Air is 0.03% $CO_2$ by volume.)
- If $CaCO_3$ is put in a chamber being pumped by a pump capable of maintaining a reduced pressure of $7.6 \times 10^{-4}$ torr, at what temperature will $CaCO_3$ decompose?

## Catalysts - & the Haber Process

$$\mathrm{N_2}(g) + 3\ \mathrm{H_2}(g) \rightleftharpoons 2\ \mathrm{NH_3}(g)$$

$$\Delta H^\circ = -92.22 \text{ kJ};\ \Delta S^\circ = -198.75 \text{ J/K}$$

- The role of a catalyst is to increase the rate of reaction (both forward and reverse rates).
- Under a given set of conditions, this has NO EFFECT on the final equilibrium state (though the system can reach equilibrium faster).
- As a practical matter in the Haber process, the catalyst allows one to use lower temperatures because equilibrium can be achieved faster.
- What is the thermodynamic benefit of running the Haber process at a lower temperature?